



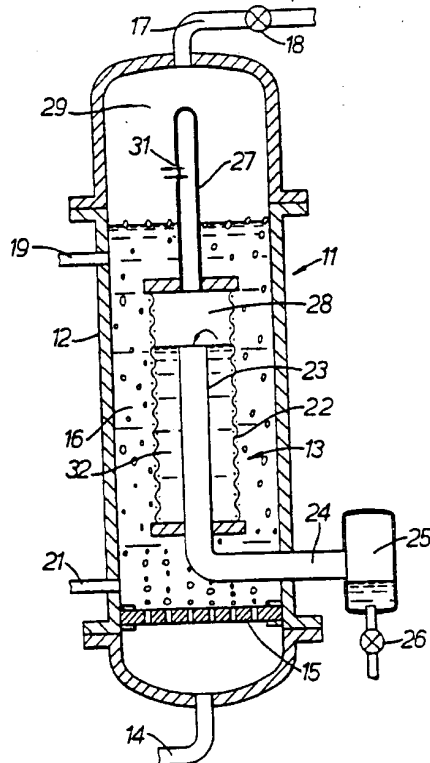
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/NO93/00031 (22) International Filing Date: 24 February 1993 (24.02.93) (30) Priority data: 9203959.3 25 February 1992 (25.02.92) GB (71) Applicant: DEN NORSKE STATS OLJESELSKAP A.S. [NO/NO]; Postboks 300 Forus, N-4001 Stavanger (NO). (72) Inventors: RYTTER, Erling ; Steinasen 19, N-7049 Trond- heim (NO). LIAN, Petter ; Alv Sciefloes veg 8, N-7058 Trondheim (NO). MYRSTAD, Trond ; Sildrapeveien 28G, N-7048 Trondheim (NO). ROTERUD, Per, T. ; Lokes vei 1, N-3690 Stathelle (NO). SOLBAKKEN, Age ; Nils Ryjordsvei 1, N-7020 Trondheim (NO).		(74) Agent: TANDBERGS PATENTKONTOR AS; Postboks 7085H, N-0306 Oslo (NO). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published With international search report.

(54) Title: METHOD OF CONDUCTING CATALYTIC CONVERTER MULTI-PHASE REACTION

(57) Abstract

A method of conducting a continuous multi-phase catalytic reaction such as the conversion of syngas to higher hydrocarbon fuels. Gaseous reactants are introduced via a gas permeable plate (15) into a slurry (16) which includes the product and a finely divided catalyst. The liquid product is separated from the remainder of the slurry by means of a filter unit (13) including a filter member (22). A pressure differential is established across the filter member (22) by means of a constant level device (23) within the filter unit which maintains a level of filtrate (32) within the filter unit (22) below the level of the slurry (16). The slurry (16) is maintained in a constant state of agitation by the introduction of the gaseous components as a stream of bubbles. Fluctuations in the pressure differential across the filter member (22) prevent the filter member from clogging, and the gas space (28, 29) is above the filtrate (32) and the slurry (16) are in communication.



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METHOD OF CONDUCTING CATALYTIC CONVERTER
MULTI-PHASE REACTION

The present invention relates to a method of conducting a continuous multi-phase catalytic reaction and is particularly, though not exclusively, applicable to the catalytic conversion of syngas, produced by the reforming of methane, to hydrocarbon fuels, by a Fischer-Tropsch type of synthesis. Other reaction systems to which the method is applicable include various slurry reactions for the production of petrochemicals, the production of oxygenates from synthesis gas and dehydrogenation reactions.

Three-phase catalytic reaction systems are used in a number of chemical processes and their application in the petrochemical industry appears to be increasing. Of the three-phase systems in use, mechanically agitated, loop and bubble column slurry reactors contain small catalyst particles dispersed in the liquid. In most applications, the liquid will have to be separated from the slurry to remove liquid products or for catalyst regeneration purposes. In those cases where the liquid is an inert medium, occasionally, it may have to be replaced due to degradation or the build-up of impurities.

Mechanically agitated slurry reactors are particularly convenient for batch process due to the low mass-transfer and heat resistance. These features also make them suitable for the determination of reaction kinetics in the laboratory. A serious disadvantage and limitation of this reactor type,

however, is the difficulty in the separation of catalyst particles in any continuous operation.

Commercially, it is only mechanically agitated reactors that are used in the hydrogenation of double bonds in oils from cottonseed, soybean, corn, sunflower etc. By employing a nickel catalyst, the products include margarine, shortening, soap and greases. The choice of reactor is based on the low diffusivities and high viscosities of the fatty oils. Fixed-bed operation has been proposed due to the advantage of completely catalyst-free products without filtration. A number of other hydrogenation reactions are also carried out in agitated reactors, e.g. the hydrogenation of nitrocompounds.

The operation of bubble column slurry reactors is simple, since mechanically moving parts are avoided. Combined with the low diffusional resistance and efficient heat transfer, these reactors are attractive for many industrial processes. However, solid-liquid separation is usually performed outside the reactor in elaborate filtering and settling systems. The catalyst slurry is to be recycled to the reactor, sometimes with the use of a slurry pump. Thus, serious problems may be encountered in the continuous operation of bubble column slurry reactors.

As world oil resources diminish it is becoming more attractive to use natural gas as an energy source and methods of upgrading this to higher hydrocarbon fuels are increasing in importance.

It is therefore an object of the invention to provide a continuous method of conducting a multi-phase catalytic reaction which does not suffer the drawbacks of the prior art.

It is a particular object of the invention to provide such a process which is well suited to use in the conversion of natural gas via syngas to diesel fuel.

According to the invention, there is provided a method of conducting a continuous multi-phase catalytic reaction in which the product includes at least one liquid component and the catalyst is a finely divided solid, the method comprising: introducing reactants into a slurry of reactants, product and catalyst in a reactor vessel; separating the liquid product from the remainder of the slurry by means of a filter member; establishing a mean pressure differential across the filter member; causing fluctuations or oscillations about the mean pressure differential; and maintaining the slurry in state of constant agitation by introducing gaseous components into the slurry as a stream or swarm of bubbles.

Such a method is relatively simple yet effective. The separation step, generally considered to be particularly problematic, is achieved without undue complication and under proper operating conditions the filter member is self-cleaning.

The reactants may be CO and H₂, for example from the reforming of methane. The reaction may then be a catalytic conversion by a Fischer-Tropsch synthesis, producing methanol and higher hydrocarbons.

Preferably, the gaseous components include any gaseous reactants. Preferably, the slurry is maintained in a turbulent state by the gas bubbles.

Preferably, a pressure differential is achieved by applying an excess pressure to the slurry side of the filter member and/or by applying a negative pressure to

the product (filtrate) side of the filter member. Preferably, the pressure differential is achieved, at least in part by maintaining the slurry at a level above the level of the product on the filtrate side of the filter member, by means of a constant level device on the filtrate side of the filter member. The pressure differential should not be allowed to increase beyond a fairly low maximum limit since the filter unit would otherwise tend to clog. Preferably, communication between the space above the slurry and the space above the filtrate prevents the build-up of pressure differentials in excess of that corresponding to the hydrostatic pressure.

The pressure fluctuations or oscillations may be achieved in various ways. The pressure fluctuations or oscillations may be carried out by the turbulent motion of the slurry in the reactor and/or by gas bubbles rising on the outside of the member, which may themselves give rise to turbulent flow conditions. This may be transferred or enhanced perhaps by resonance effects to the filtrate, preferably by way of communication between the gas volume above and the slurry and the gas volume above the filtrate. Alternatively, the pressure fluctuation may be achieved by applying a pulsating pressure to the gas volume above the filtrate.

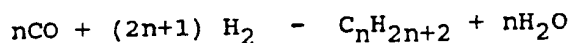
The pressure fluctuation value may be of the order of the pressure differential, for example from 10 to 200% of the pressure differential. The actual value of the pressure differential may be from 1 to 1000mBar, preferably 2 to 50mBar. Very good operational results may be obtained in the range of 2 to 10mBar in the case of a Fischer-Tropsch conversion of syngas to

hydrocarbon products.

The filter member is preferably in the form of a filter unit which defines internally the filtrate zone and which includes a filter element separating the filtrate from the slurry. Preferably the filter element is generally cylindrical and its axis is generally vertical in use though it may be inclined by as much as 10° or even 30° to the vertical. The member material and catalyst are preferably selected so that the maximum hole or pore size in the filter element is of the same order of magnitude as the catalyst particle size, the particle size preferably being not less than half the pore size. However, it would be possible for the catalyst particle size to be larger than the maximum pore size, with the pore size being of the same magnitude or less.

The invention also extends to a method of converting natural gas (methane) to higher hydrocarbon fuels which involves initially reforming the methane to produce carbon monoxide and hydrogen, subjecting the CO and H_2 to catalytic conversion by a Fischer-Tropsch synthesis using the method mentioned above to form higher hydrocarbon fuels such as liquid paraffin waxes, and subsequently separating and/or cracking these products to produce the required range of hydrocarbons.

The mechanism of the Fischer-Tropsch synthesis is probably quite complicated but the formation of hydrocarbons can be summarised as follows:-



A preferred catalyst and process is described in

EP-A-313375.

When diesel fuel is produced in this way it is vastly superior to conventional diesel in terms of its quality and properties. Firstly, it contains no sulphur or aromatics, which is important from an environmental point of view. Secondly, it has a very high cetane number and can therefore be blended with lower grades of diesel fractions in order to give a product which meets premium range standards. Thirdly, it contains virtually no harmful compounds that generate soot when burned and needs fewer additives for problem free use at low temperatures.

The invention may be carried into practice in various ways and some embodiments will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a schematic section through a three-phase slurry reactor for performing a method in accordance with the invention;

Figure 2 is a simplified schematic section through a part of a reactor showing an alternative system for achieving the fluctuations in pressure;

Figures 3, 4 and 5 are views similar to Figure 2 showing three ways of adjusting the pressure differential across the filter member.

Figures 6 and 7 are views similar to Figures 3 to 5, showing two further variants.

The reactor vessel 11 in Figure 1 comprises an outer casing 12 defining the reactor vessel 11 and within the casing 12 a filter unit 13. The housing 12 has a gas inlet 14 at the bottom which, in the case of a syngas conversion process, would constitute the reactant inlet. Above the gas inlet 14, there is a gas

delivery device such as a gas-permeable frit plate 15 which supports the slurry 16 in the reactor vessel 11, and at the top of the casing 12, a gas outlet 17. The gas outlet 17 is controlled by a choke or valve 18. The casing also has an inlet 19 and an outlet 21 for the slurry.

The filter unit 13 comprises a generally vertical cylindrical filter element 22 in contact with the slurry 16. The filter element is in the form of a fine meshed screen though it could alternatively comprise helically wound metal threads, sintered metal particles or narrowly separated fine vertical threads. It houses a constant level device in the form of a vertical pipe 23 which terminates below the top of the filter unit 13. The pipe 23 leads to a filtrate outlet 24 which in turn leads to a collector 25 and to an outlet valve 26. A tube 27 extends from the space 28 within the filter unit 13 above the top of the pipe 23 to the space 29 within the top of the reactor 11 above the filtrate 16. An opening 31 in the tube 27 connects the two spaces 28,29.

In operation, gaseous reactants are introduced to the reactor vessel 11 via the inlet 14 and the plate 15. The reactants form bubbles in the slurry 16 which pass upwards past the filter unit 13. The slurry 16 consists of a liquid phase of the reaction products and a catalyst in finely divided form. The gaseous reactants react as they contact the catalyst, thus adding to the products in the slurry.

At the same time, the products pass through the filter element 22 to form a product filtrate 32 which is free of catalyst. Any gaseous products and unreacted reactants can be vented through the outlet 17

and subsequently treated and/or recycled. The product filtrate 32 leaves the filter unit 13 via the constant level device 23 and outlet 24 and is collected in the collector 25 for regulated continuous or periodic removal.

The difference in level between the slurry 16 and the product filtrate 32, determined by the constant level device, results in a pressure differential across the filter element 22. This helps to convey the liquid product through the filter element 22.

It might be expected that, under these conditions, the catalyst would clog the filter element, however, this is found not to be the case, provided that the pressure differential is not too great. The introduction of the reactants together with the connection of the gas spaces 28, 29, and the generally turbulent conditions in the reactor vessel 11 combine to cause fluctuations in the pressure differential across the filter element 22. These in turn cause fluctuations in the liquid flow through the filter element 22 resulting in an anti-clogging effect. This may be enhanced by the movement of the gas bubbles past the surface of the filter element 22.

An alternative embodiment is shown in Figure 2. In this case the filter unit 41 has no tube 27 connecting the space 28 to the space 29 in the reactor (not shown). Instead, a cylinder and piston assembly 42 is connected to the space 28. By reciprocating the piston, a pulsating pressure is produced resulting in the desired fluctuation in the pressure differential across the filter element 22. This arrangement can of course be used in conjunction with the embodiment shown in Figure 1. Communication between the spaces above

the slurry and the filtrate may be provided by a tube (not shown) having a restriction or choke limiting the transmission of pressure pulses to the space above the slurry, which would otherwise have tended to eliminate the net effect of the reciprocating piston. The tube would nevertheless control the static pressure differential.

The constant level device 23 can be made adjustable in order to provide a degree of control over the pressure differential across the filter element 22. Three ways in which this can be achieved are shown in Figures 3, 4 and 5.

In the filter unit 51 of Figure 3, both the vertical pipe 52 and the tube 53 are slidably mounted with respect to the filter unit 51. In the filter unit 61 of Figure 4, the vertical pipe 62 is slidably mounted but the tube 63 is fixed relative to the filter unit 61. In the filter unit of Figure 5, the tube 73 is fixed, and the vertical pipe 72 is slidably mounted within a fixed sleeve 74. Thus, the level of the filtrate 32 remains fixed relative to the filter unit 71 as it is raised or lowered.

The variants shown in Figures 3 to 5 can be combined with either of the embodiments shown in Figures 1 and 2.

In the reactor 81 shown in Figure 6, the outlet 84 from the filter unit 83 has an upward loop 85 to ensure that the filter unit 83 is filled with liquid. In the reactor 91 shown in Figure 7, there is a tube 97 connecting the gas space in the reactor to the filtrate. The outlet 94 extends to the bottom of the filter unit 93 and there is an optional connection 96 between the outlet 94 and the space in the reactor.

This connection 96 would tend to prevent any siphon effect and allow any gas remaining in the filtrate to escape. Again, the filter unit 93 will be filled with filtrate.

In all the illustrate embodiments, the geometries of the reactor, the communication means (eg. the tube 27) and the filtrate section may be varied in size and in order to optimise the pressure fluctuations by exploiting resonance-like effects.

The invention will now be further illustrated in the following Examples which were conducted on a laboratory scale.

EXAMPLE I

A stainless steel tube, with a diameter of 4.8cm and a height of approximately 2 meters was filled with a hydrocarbon liquid and a fine powdered catalyst. The tube was operated as a slurry bubble column by bubbling gas through the slurry.

A filter unit was placed in the upper part of the reactor. The filter unit was made of Sika stainless steel sintered metal cylinder Type R20 produced by the company Pressmetall Krebsöge GmbH. The filter unit had an outer diameter of 2.5cm, a height of 25cm, and an average pore size of 20 μm .

In this particular experiment, the reactor was filled with a slurry consisting of a poly α -olefin liquid and approximately 10 weight % of a fine powdered cobalt on alumina catalyst. The particle size ranged from 30 to 150 μm . The catalyst was kept suspended by gas bubbling through the liquid. The gas was a mixture of H_2 , CO and N_2 of varying composition, and was fed with a superficial gas velocity of 4cm/s. The temperature in the reactor was 230°C, and the pressure

was 30 bar (3×10^6 Pa).

The filtrate level inside the slurry was set approximately half way up in the valve.

The liquid formed by the Fischer-Tropsch reaction in the reactor was withdrawn through the filter unit. In addition, a poly α -olefin liquid fed to the reactor was also withdrawn through the filter unit. The liquid withdrawal varied from 320 to 2.5 g/h depending on the formation rate of the liquid product, and the feeding rate of the hydrocarbon liquid. The experiment lasted approximately 400 hours, and a total amount of liquid of 30 litres was withdrawn through the filter unit. The liquid level in the reactor was constant during the experiment, and no colour indicating presence of solid particles could be observed in the liquid.

EXAMPLE II

A glass tube, with a diameter of 22cm and a height of 2.5 meters was filled with hydrocarbon liquid (Monsanto heat transfer fluid, MCS 2313) and a fine alumina powder (average particle diameter approximately 75 μ m). The content of alumina was approximately 15% by weight. The tube was operated as a slurry bubble column (SBC) by bubbling gas through the slurry.

A filter member without a connection tube between the gas volume above the slurry phase and the gas volume above the product phase was placed in the upper part of the SBC. The filter member was made of a Sika fil 10 stainless steel sintered metal cylinder produced by Sintermetallwerk Krebsöge GmbH. The sinter cylinder had an outer diameter of 2.5cm, a height of 20cm, and an average pore size of 10 μ m.

In this particular experiment the slurry level was set to be at the top of the sinter cylinder. The

pressure amplitude in the SBC was measured to be 6mBar, the pressure drop across the sinter metal wall was approximately 3-4 mBar (300-400Pa). The temperature in the slurry was 20°C, the pressure was 1 Bar (10⁵Pa) and the gas velocity was approximately 6cm/s.

At the start of the experiment, the flow of the filtrate through the sinter metal cylinder was about 1000ml per minute. After 4 hours the flow was reduced to zero due to clogging of the sinter metal wall on the slurry side.

When a similar experiment was carried out in an apparatus in which communication between the gas volumes was provided by a piece of pipe acting as a connection tube, the initial flow rate was maintained essentially at the same level throughout the experiment.

CLAIMS

1. A method of conducting a continuous multi-phase catalytic reaction in which the product includes at least one liquid component and the catalyst is a finely divided solid, the method comprising: introducing reactants into a slurry (16) of reactants, product and catalyst in a reactor vessel (11), characterised by: separating the liquid product (32) from the remainder of the slurry (16) by means of a filter member (13); establishing a mean pressure differential across the filter member (13); causing fluctuations or oscillations about the mean pressure differential; and maintaining the slurry (16) in state of constant agitation by introducing gaseous components into the slurry (16) as a stream of bubbles.
2. A method as claimed in Claim 1, characterised in that the gaseous components include any gaseous reactants.
3. A method as claimed in Claim 1 or Claim 2, characterised in that the slurry (16) is maintained in a turbulent state by the gas bubbles.
4. A method as claimed in any preceding Claim, characterised in that the pressure differential is achieved, at least in part by maintaining the slurry (16) at a level above the level of the product (32) on the filtrate side of the filter member (13), optionally by means of a constant level device on the filtrate

side of the filter member (13).

5. A method as claimed in any preceding Claim, characterised in that the fluctuations or oscillations are caused by the turbulent motion of the slurry (16).

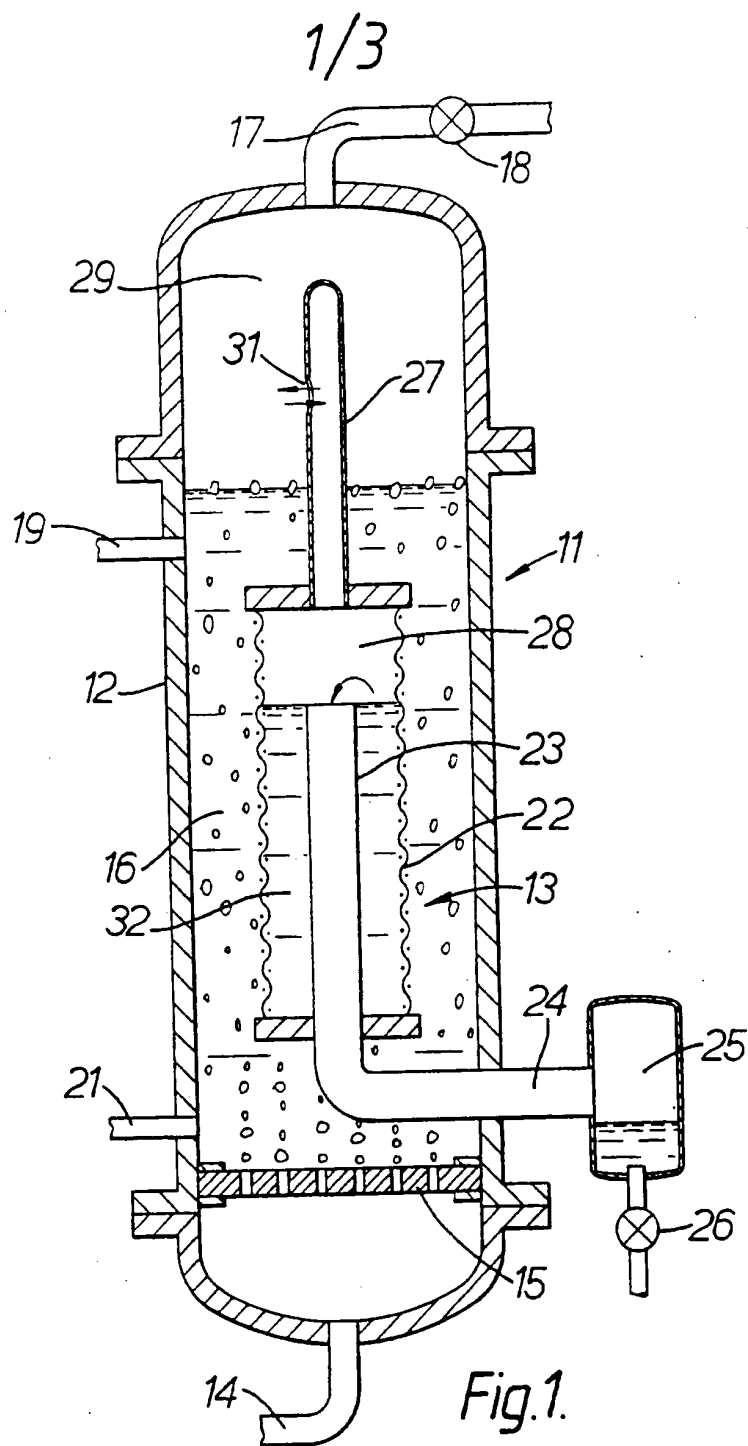
6. A method as claimed in any preceding Claim, characterised in that the fluctuations or oscillations are achieved by applying a pulsating pressure to the gas volume (28) above the filtrate (32).

7. A method as claimed in any preceding Claim, characterised in that a gas space (29) above the slurry (16) is in communication with the filtrate (32) or any gas space (28) above the filtrate (32).

8. A method as claimed in any preceding Claim, characterised in that the mean differential pressure is less than 500 Pa.

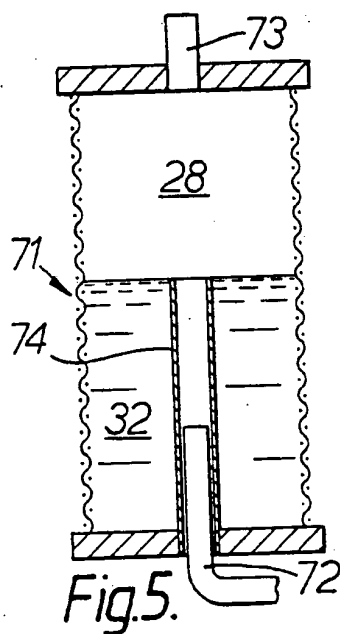
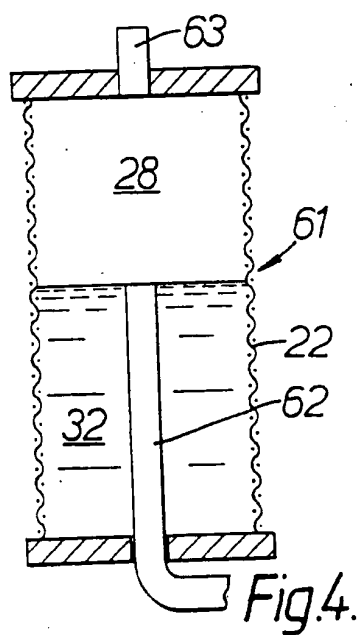
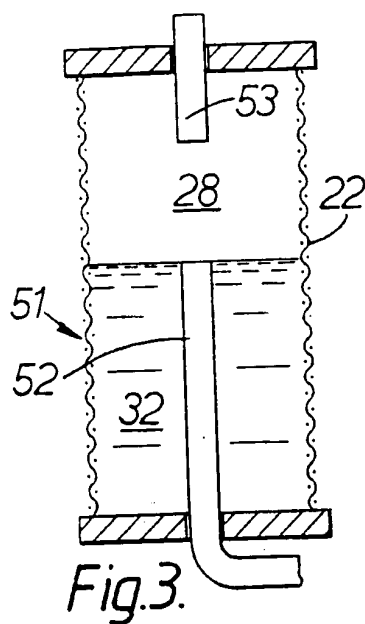
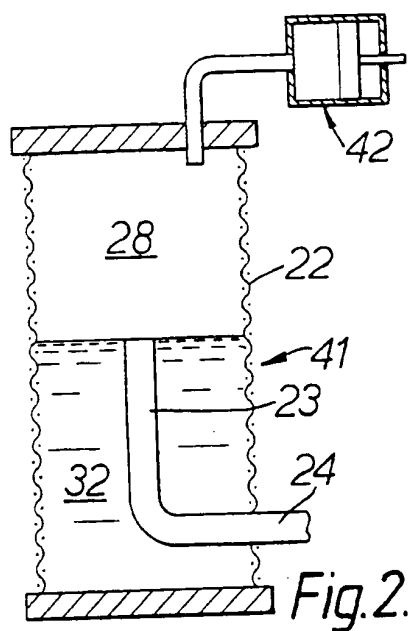
9. A method as claimed in any preceding Claim, characterised in that fluctuations or oscillations are in the range of from 10% to 200% of the mean pressure differential.

10. A method as claimed in any preceding Claim, characterised in that the reactants are CO and H₂, the catalyst is a Fischer-Tropsch catalyst and the products are methanol and higher hydrocarbons.

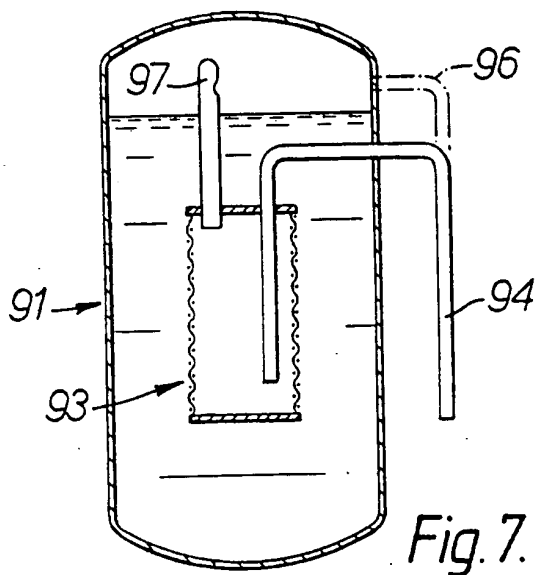
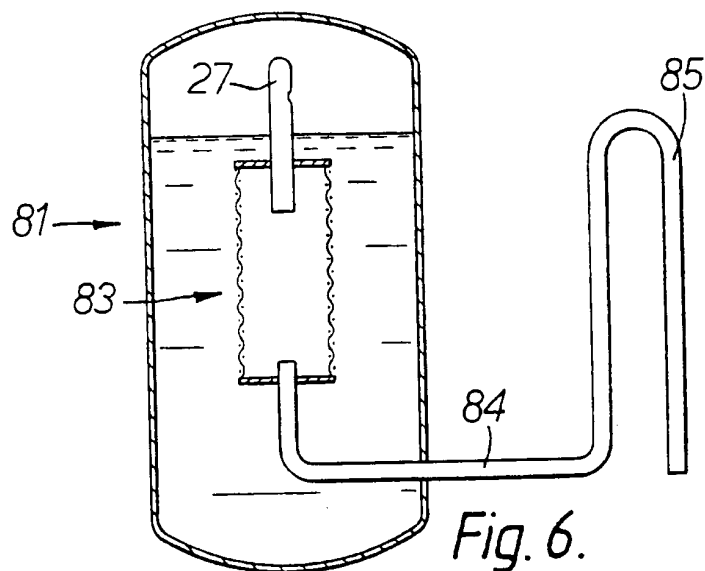


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INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 93/00031

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: B01J 8/22, C07C 1/04, C10G 2/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B01J, C07C, C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0450859 (EXXON RESEARCH AND ENGINEERING COMPANY), 9 October 1991 (09.10.91) --	1
A	EP, A2, 0450860 (EXXON RESEARCH AND ENINGEERING COMPANY), 9 October 1991 (09.10.91) --	1
A	EP, A2, 0450861 (EXXON RESEARCH AND ENGINEERING COMPANY), 9 October 1991 (09.10.91) -----	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

24 May 1993

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Name and mailing address of the ISA/
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Facsimile No. +46 8 666 02 86

Authorized officer

Jack Hedlund
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

31/03/93

International application No.
PCT/NO 93/00031

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0450859	09/10/91	AU-B- 632412	24/12/92
		AU-A- 7401491	10/10/91
		US-A- 5157054	20/10/92
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		AU-A- 7401591	10/10/91
EP-A2- 0450861	09/10/91	AU-A- 7401791	10/10/91